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APPLICATION OF A TWO-STREAM RADIATIVE TRANSFER MODEL FOR LEAF LIGNIN AND CELLULOSE CONCENTRATIONS FROM SPECTRAL REFLECTANCE MEASUREMENTS (PART 1).

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- 1. Introduction. Lighin and nitrogen contents of leaves constitute the primary rate-limiting parameters for the decomposition of forest litter, and are determinants of nutrient itude carbon cycling rates in forest ecosystems (Melillo, et al., 1982). Wessman et al (1988a) developed empirical multivariate relationships between forest canopy lighin amount and the (first-difference) AIS spectral response in a time bands spread over the wavelength interval 12s61sss nm. Wessman et al (1988b) and McLellan et al (1991) developed similar regression relationships from laboratory reflectance measurements on dried samples prepared in a standard fashion. They used four to six infrared bands for analysis of nitrogen, lighin and *1Iu1osc content of foliage in forest and prairie species. In the present paper the feasibility of compositional determinations is explored using positions of composite absorption hands that originate from mixtures of lighin, cellulose, and possibly other chemical constituents in the spectral reflectance of green leaves. To carry out this program, 'WC employ full spectral resolution single leaf diffuse reflectance measurements made with a laboratory spectrometer and integrating sphere, The leaf and other chemical reflectance data compiled by Elvidge (1989) have also been utilized extensively,
- 2. Model. The spectra of fresh leaves contain strong liquid water absorption that may mask nearly completely the spectral signatures of other leaf chemical constituents (e.g., Elvidge, 1989). A background liquid leaf water reflectance spectrum is required to remove the effects of liquid water, Previously, such a background spectrum was estimated using mix-of glass beads and liquid water (Goetz, et at. 1990). In the present work us the other hand, the so-called Kubelka-Munk (KM) theory of radiative transfer (Wendlandt and Hecht, 1%6) was used to estimate the liquid water spectrum from the leaf diffuse spectral reflectance itself. In a first approximation single leaves are assumed to consist of distinct but well-mixed liquid water and dry components each characterized by intrinsic absorption (k., k.) and scattering (s., s.) functions (hereafter simply intrinsic functions). The dry components are in turn assumed to consist of well-mixed lignin, cellulose, starch, protein, and other organic compounds (see Elvidge, 1989, for representative visible and near-infmwd spectra). In the KM theory, which was originally developed to calculate the reflectance of paint films, independent as well as purely backward scattering (van de Hulst, 1980) are assumed by all constituents. These assumptions are almost certainty violated to one extent or another In leaves. Comparing the k- and s-functions of KM theory with parameters of Iwo-strewn atmospheric models (see, for example, Coakley and Chylek, 1975) shows k to & identified 'with particle absorption, given by 1 - To, where To is the single scattering albedo, and s with the scattered fraction $\varpi_0 \beta$, whore β is the average forward scatter for isotopically incident radiation (Wiscombe and Grams, 19?6),
- 3. Calculation of k- and s-functions. We develop mixing laws that comprise relationships between bulk leaf scattering (S) and absorption (K) functions and the intrinsic functions of assumed individual components; the bulk functions are simple linear sums of the intrinsic functions weighted by constituent concentrations (c_w, c_d). For a simple two-component system, the intrinsic functions are isolated individually by use of reflectance (R) and transmittance (T) measurements on single leaves, both wet and desiccated, together with theoretical relationships for R and T for single uniform layers from KM theory (Wendlandt and Hecht, 1966, p. 60), Allen and Richardson (1968) first used single leaf R and T data to calculate k-and s-coefficients for cotton leaves, The intrinsic functions derived in this way for Liquidambar styraciflua (sweetgum) are given in Figure 1,
- 4. Leaf water reflectance. Given k, and SW of Figure 1, the reflectance R, of a semiinfinte body of "pure" liquid leaf water was calculated from the so-called KM remission function (Kortum, 1969, p.180, discusses the remission function). A light path through a stack of 5 or 6 leaves approximates an infinite thickness condition at all wavelengths between 400-2500 nm, since no change in reflectance occurs with addition of further layers. The resulting R, is shown in Figure 2. The function represented hits been smoothed once by a three-point "hanning"

filter (Blackman and Tukey, 1958) to suppress fluctuations in the calculated k- and s-functions from noise in the reflectance data themselves. The curve of Figure 2 has been taken arbitrarily to represent a generic background water reflectance for derivation of dry constituent spectral residuals from the optically infinite thickness green lenf diffuse reflectance. An example comparing R_m with the equivalent semiinfinite reflectance for sweetgum, calculated from K and S via the remission function, is shown in Figure 3. Both curves have been translated to zero reflectance at 1452 nm, and the water reflectance adjusted by a single scale factor to achieve the match shown. Similar adjustments of origin and scale in R_m were required in calculation of residuals for foliage of other species as described next.

- 5. Reflectance residuals. We calculated fractional residual reflectances for sweetgum, sycamore (Platanus racemosa), pinyon pine (Platanus monophylla) and bigberry manzanita (Arctostaphylos glauca) using the generic water reflectance curve. These results are given in Figure 4 for the spectral region 1400-1900 nm. The fractional residual reflectance is defined as $1 (R_m R_m)/R_m$, where. ~isthemeasured (~uiated) reflectance for infinite thickness of species i. The diffuse reflectance data for sycamore, pinyon pine, and manzanita were taken from Elvidge (1989). These examples are distinguished from one another by apparent systematic displacements of reflectance minima from one species to the next and by the premed ~mqjor& tr*inwa twt.umaintha pinyon and manzanita residuals that are not shared by the other examples, The noise-equivalent reflectance variation (neAR) in these data was estimated numerically by calculating residuals from a second degree polynomial fit to a smooth piece of the raw sweetgum reflectance (1500-1600 nm, 24 points) with resulting residuals are reflectance Units and average fractional uncertainty of 0.000001.
- 6. Comparison of dessicated leaf and residual spectra, From the derived k_d and s_d values given in Figure 1 we also calculated the expected reflectance R_{dm} for dessicated sweetgum via the remission function, and compared structure in that reflectance with structures present in the (presumed liquid water-free) residual spectrum for sweetgum in Figure 3, This comparison is made in Figure 5, Apart from positions of minor features these curves do not resemble one another; the presence of important (lignin + cellulose + other) absorptions remains masked in the extracted residual spectrum. Features in the calculated sweetgum spectrum R_{dm} are, on the other hand, present in the pinyon and manzanita residuals in Figure 4.
- 7. Interpretation of dessicated leaf spectra. We next sought to understand structures in the dry extracted and derived spectra using calculated reflectances of hypothetical simple two-component mixtures. The reflectances and mixing models used, including the model employed to derive R.,... ultimately require validation; this has not yet been possible beyond certain qualitative comparisons described in Section 7.

In Figure 6 the calculated spectrum $R_{\bullet\bullet}$ is compared with lignin and cellulose reflectances (from Elvidge, 1989). A simple interpretation of band position in the desiccated leaf spectrum appears possible in terms of these two end members. We examined this more closely by calculating reflectances of cellulose-lignin and other mixtures and comparing band positions between the hypothetical mixes and $R_{\bullet\bullet}$.

Bulk reflectance relationships based on composite scattering and absorption functions were developed from the KM theory for artificial mix-of dry constituents (and liquid water with dry constituents described in Section 7). Many idealized configurations of constituents in single leaves, each individually described by the KM reflectance and transmittance formulae, seem possible. Each has its own macroscopic mixing formula Some simple possibilities are: (1) single layers comprised of well-mixed pure components, (2) multiple stacked uniform layers of pure end members, and (3) side-by-ride compartments of pure end members arranged in single layers. Here we confine attention to (1), lacking a definite basis to pursue another option. Since intrinsic functions of representative major (or minor) pure chemical end members of leaves have not yet been obtained, the development of mixing relations must proceed approximately, in the present case as follows. For two components [1,2] the ratio K₁₂/S₁₂ of a mixture is

and $c_1 + c_2 = 1$. Except for the ratio s_2/s_1 , the values of the component k/s-ratios are known from the remission function if the spectral diffuse reflectance R_{j+} for each component j is known. We will calculate an approximate effective composite ratio $K_{1/2}/S_{1/2}$ for the (1.2) mixture by setting $s_2/s_1 = 1$ for all wavelengths. and take the diffuse reflectances of leaf chemical constituents. a number of which have been measured by Elvidge (1989), to estimate

$$\frac{K_{12}}{S_{12}} = \frac{\sigma_1 \frac{K_1}{S_1} + \sigma_2 \frac{K_2}{S_2} \frac{S_2}{S_1}}{\sigma_1 + \sigma_2 \frac{S_2}{S_1}}$$
(1)

k/s-ration of end-members. In so doing effects of possible impurities, nonuniformity in packing, particle size, and, finite sample thickness on reflectances of assumed end members are ignored. The reflectance R₁₀, of a two-Component mix is calculated from

$$R_{12m} = \frac{1 - \sqrt{K_{12}/(K_{12} + 2S_{12})}}{1 + \sqrt{K_{13}/(K_{13} + 2S_{13})}}$$
 (2)

Figure 7 illustrates application of the model represented by Equation (2) to a mixture Of lignin and cellulose, parameterized as fraction of cellulose (gm/gm) in the mix. Determination of composition in this simple dry system might be made from measurement of band position; best resolved and cleared to interpret (although unobservable in the residual spectra from green leaves) is that between 1444 and 1484 nm. This band (reflectance minimum) position is a non-linear function of cellulose fraction f_{ϵ} , given accurately by $\lambda(f_{\epsilon})$. 1456 + 97.9 f_{ϵ} - 119 f_{ϵ}^{-1} + 54 f_{ϵ}^{-3} . 4.5 f_{ϵ}^{-4} , and is very insensitive to changes in lignin concentration for ... 5 $f_{\epsilon} \le 1.0$. For example, suppose the spectral sampling interval $\Delta\lambda$ is that of AVIRIS, 10 nm, and that three perfect spectral band determinations are possible at 1484 and 1474 and 1464 nm. The minimum resolvable difference in lignin concentration Δf_{ϵ} is approximately 0.75 between the first pair of these and about 0.10 between the second pair. A similar relationship, spectrally less well defined, prevails for the complex of bands between 16S0 and 1850 nm,

We return now to interpretation of band positions of R_{\bullet} , in Figure 6, From the regression formula for $\lambda(l)$ 4 reflectance minimum at 1460 nm implies a lignin concentration in the two-component dry mix of 9A%, and a similar abundance from the band near 1775 nm. This exceeds by far the expected lignin abundance in plant materials Of 10-35% dry weight (Crawford, 1981).

Other chemical constituents in addition to lignin and cellulose make spectral contributions to the desiccated foliar reflectance, and will alter by dilution the relative abundances of lignin and cellulose present. The nature of the spectral contributions so introduced will be described qualitatively using hypothetical two-component systems, cellulose-starch and cellulose-protein (D-ribulose 1-5-diphosphate carboxylase), illustrated in Figures 8 and 9. Combinions with other plant chemical constituents might be worked out from spectral data given by Elvidge (1989). The admixing of starch with cellulose displaces the 1485 run cellulose band to shorter wavelengths, similar to lignin. The 1775 nm band position is largely unaffected. The admixing of protein with cellulose produces displacements opposite (but of comparatively small magnitude) to those of both starch and lignin at 1485 nm and to shorter wavelengths at 1775 nm, also similar to that of lignin. Thus both protein and starch mimic spectrally the presence of lignin in mixes with cellulose, especially at 1775 nm. The isolation of lignin concentration from band position alone without knowledge of other end member concentrations thus seems problematical.

- 8. Mixing of dessicated and liquid water components. Mixing relationships employed in the present application of KM theory together with spectral reflectances of mixtures based thereon have been worked out to Isolate signatures of supposed desiccated leaf components and to aid interpretation of spectral signatures of derived reflectance residuals. The theory applied to leaf reflectance awaits detailed experimental validation but offers another set of relationships that suggest its usefulness. We used the intrinsic k- and s-functions of Figure 1 together with Equations (1) and (2) to calculate for sweetgum the spectral reflectance of intermediate mixtures of wet and dry components. These calculations are illustrated in Figure 10. A comparison with single leaf reflectance data as a function of relative water content given by Hunt and Rock (1989) is suggestive.
- 9. Reflectance retrieval from AVIRIS. The previous analysis leading to plots of residuals given in Figure 4 was based on diffuse spectral reflectance measurements made under idealized conditions with a laboratory spectrometer. The largest spectral variations in these residuals amount to approximately 2 % in the 1700 nm region. Reflectance variations are also present below this level. Under field conditions, using measurements of the upwelling

radiance at AVIRIS, an atmospheric model is ordinarily required to retrieve an effective surface (Lambertian) reflectance, unless ground targets can be used (Elvidge, 1988). Noise arising from spatial fluctuations or uncertaintification atmospheric properties and from AVIRIS will contribute uncertainty to the reflectance values so derived. We corried out numerical experiments with the LOWTRAN 7 (Kneizys, et al., 1983) radiative transfer model to estimate uncertainties due to atmospheric variations. It proves advantageous to recalibrate AVIRIS inflight using local surface targets to eliminate channel to channel variations in radiance that are thought to originate from changes in the radiometric calibration coefficients between laboratory and inflight conditions.

For homogeneous, plane-parallel atmospheric conditions over uniform ground of Lambertian surface reflectance p_a, the radiance at AVIRIS is represented approximately as

$$L(\mu, \mu_0, \tau) = \frac{P_0}{4\mu} \left[S(\mu, \mu_0, \tau) + \frac{4\rho_T}{1 - \rho_{gB}} \mu \mu_0 T(\mu, \mu_0, \tau) \right]$$
 (3)

In Equation (3) πF_0 is the solar irradiance, $S(\mu, \mu_0, \tau)$ is the atmospheric scattering function. $T(\mu, \mu_0, \tau)$ is the two-way diffuse plus direct atmospheric transmittance, s is the. hemispherical backscatter function, μ and μ_0 are cosines of the zenith angles of viewing and solar incidence directions respectively, and τ is optical depth. Spectral dependence of the atmospheric and surface quantities is implied. An inflight calibration experiment redefines the radiometric calibration in terms of inflight coefficients Φ^* given by

$$\Phi^{\bullet} \cdot \frac{\langle L_{N} \rangle_{c}}{\langle DN - DN_{0} \rangle_{c}} \tag{4}$$

where DN and DN₀ represent instrument and dark current response for the conditions of calibration, and (L_m), is the radiance at AWNS obtained from a radiative transfer model (LOWTRAN and/or MODTRAN) using measured atmospheric conditions. (L_m), is given approximately by

$$(L_{a})_{a} = \left[\frac{s_{a}}{4\mu_{a}} + (\mu_{0})_{c} T_{c} R_{c} + (\mu_{0})_{c} T_{c} \overline{s}_{c} R_{c}^{a} \right] P_{0}$$
 (5)

With the inflight calibration factors, the ground reflectance R, is

$$R_{\overline{B}} = -\frac{\overline{A}}{B} - \overline{S} \left(\frac{\overline{A}}{B} \right)^2 + \left[1 + 2\overline{S} \left(\frac{\overline{A}}{B} \right) \right] \frac{\Phi^*}{B} (DN - DN_0) - \overline{S} \frac{\Phi^{*2}}{B^2} (DN - DN_0)^2$$
 (6)

where (DN - DN_b) represents the dark-current corrected inflight instrument response, and

$$A = \frac{SF_{\odot}}{4u}$$
, $B = \mu_{\odot}TF_{\odot}$

The expression for R_p . Equation (6) is independent of the solar irradiance, but use of the inflight calibration CO@UWW90" has introduced additional variables pertaining to atmospheric conditions during calibration and also the calibration target reflectance R_p . We applied standard error propagation formulas to Equation (6) to evaluate a fractional uncertainty G_{np}/R_p from fluctuations in all the atmospheric parameters (taken equal for both calibration and observation experiments) and from the AVIRIS response parameterized as the signal/noise ratio. The LOWTRTAN model evaluated was midiatitude summer, rural acrosols, surface meteorological range 25 km, surface reflectance 030, and solar zenith angle 22° , 179. The calculated uncertainty as a function of AVIRIS signal/noise ratio at 17(1) nm with prescribed atmospheric uncertainties, written collectively as σ_p/a to represent σ_p/a , etc., are shown in Figure 11. Values of σ_{np}/R_p less than a few percent are achieved only for uniform atmospheric conditions ($\sigma_p/a < .01$) and high signal/noise ratios (>100).

10. Summary. We used the Kubelka-Munk theory of diffuse spectral reflectance in layers to analyze influences of multiple chemical components in leaves. As opposed to empirical approaches to estimation of plant chemistry, the fall spectral resolution of laboratory reflectance data was retained in an attempt to estimate lighting

or other constituent concentrations from spectral band positions. A leaf water reflectance spectrum was devised from theoretical mixing rules, reflectance observations, and calculations from theory of intrinsic k- and s-functions. Residual reflectance bands were then isolated from spectra of fresh green leaves. These proved hard to interpret for composition in terms of simple two component mixtures such as lignin and cellulose. We next investigated spectral and dilution influences of other possible components (starch, protein). These components, among others, added to cellulose in hypothetical mixtures, produce band displacements similar to lignin, but will disguise by dilution the actual abundance of lignin present in a multicomponent system. This renders interpretation of band positions problematical. Knowledge of end-members and their spectra, and a more elaborate mixture analysis procedure may be called for (see, for example, Kortum, 1969, p. 303), Good observational atmospheric and instrumental conditions and knowledge thereof are required for retrieval of expected subtle reflectance variations present in spectra of green vegetation.

11. Acknowledgments. We thank Chris Elvidge of Desert Research Institute, Reno. Nevada, for use of his This paper presents results of research at Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA. () Site of the with Dr. Rarry Prigger, Botany 12. References. 12, References.

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- Figure 1. L. styracifiua. (a) intrinsic functions for leaf liquid water component. (b) intrinsic functions for bulk denticated leaf components.
- Figure 2. L. styracifina leaf liquid water reflectance calculated from k, and s, P@11r83..Lk#- reflectance R. compared to the infinite thickness reflectance of L. Styraciflua.
- Figure 4. Reflectance residuals for fresh leaves and needles of four plant species.
- Figure 5. Comparison of the calculated dessicated leaf reflectance for L styraciflua with its fresh leaf reflectance residual.
- Figure 6. Reflectances of lignin, cellulose, and dessicated L. styractiflua.

 Figure 7. Reflectances of hypothetical mixes of cellulose and lignin. Curves are for cellulose fractions of 1.0: callulose). 0,9,0.8,0.6, 0.4, 0.2, and 0.0 (pure lignin).
 - Figure 8. Reflectances of hypothetical mixes of cellulose and starch. See caption Figure 7 for curve assignments. F@89. Reflectances of hypothetical mixes of cellulose and protein. See caption Figure 7 for curve assignments.
- Figure 10. Reflectances of hypothetical combinations of dessicated L. styraciflua and leaf liquid water components.
- Figure 11. Calculated uncertainties in retrieved surface reflectance for AVIRIS S/N and atmospheric variability.

APPLICATION OF A TWO-STREAM RADIATIVE TRANSFER MODEL FOR LEAF LIGNIN ANI) CELLULOSE CONCENTRATIONS FROM SPECTRAL REFLECTANCE MEASUREMENTS (PART 2)

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1. Interpretation of desiccated leaf spectra, Continuing the work described in Part 1, we next sought to understand structures in the dry extracted and derived spectra using calculated reflectance of hypothetical simple two-component mixtures. The reflectance and mixing models used, including the model employed to derive $R_{w\infty}$, ultimately require validation; this has not yet been possible beyond certain qualitative comparisons described here,

In Figure 1 the calculated spectrum $R_{d\infty}$ is compared with lignin and cellulose reflectance (from Elvidge, 1990). A simple interpretation of band position in the desiccated leaf spectrum appears possible in terms of these two end members. We examined this more closely by calculating reflectance of cellulose-lignin and other mixtures and comparing band positions bet ween the hypothetical mixes and $R_{d\infty}$.

Bulk reflectance relationships based on composite scattering and absorption functions were developed from the KM theory for artificial mixtures of dry constituents (and liquid water with dry constituents described here). Many idealized configurations of constituents in single leaves, each individually described by the KM reflectance and transmittance formulae, seem possible, Each has its own macroscopic mixing formula. Some simple possibilities are: (1) single layers comprised of well-mixed pure components, (2) multiple stacked uniform layers of pure end members, and (3) side-by-side compartments of pure end members arranged in single layers. Here we confine attention to (1), lacking a definite basis to pursue another option, Since intrinsic functions of representative major (or minor) pure chemical end members of leaves have not yet been obtained, the development of mixing relations must proceed approximately, in the present case as follows. For two components $\{1,2.\}$ the ratio K_{12}/S_{12}

$$\frac{K_{12}}{S_{12}} = \frac{c_1 \frac{k_1}{s_1} + c_2 \frac{k_2}{s_2} \frac{s_2}{s_1}}{c_1 + c_2 \frac{s_2}{s_1}}$$
(1)

of a mixture is and $c_1+c_2=1$. Except for the rat io s_2/s_1 , the values of the component k/s-ratios are known from the remission function if the spectral diffuse reflectance $R_{j\infty}$ for each component j is known, We will calculate an approximate effective composite ratio K_{12}/S_{12} for the $\{1,2\}$ mixture by setting $s_2/s_1=1$ for all wavelengths, and take the diffuse reflectance of leaf chemical constituents, a number of which have been measured by Elvidge (1990), to estimate k/s-ratios of end-members. In so doing effects of possible impurities, nonuniformity in packing, particle. size, and finite sample thickness on reflectance of assumed end members are ignored, The reflectance $R_{12\infty}$ of a two-component mix is calculated from Figure 2 illustrates application of the model represented by Equation (2) to a mixture of lignin and cellulose parameterized as fraction of cellulose (gm/gm) in the mix. Determinat ion of

$$R_{12*} = \frac{1 - \sqrt{K_{12}/(K_{12} + 2S_{12})}}{1' + \sqrt{K_{12}/(K_{12} + 2S_{12})}}$$
(2)

composition in this simple dry system might be made from measurement of band position; best resolved and clearest to interpret (although unobservable in the residual spectra from green leaves) is that between 1444 and 1484 nrn. This band (reflectance minimum) position is a non-linear function of cellulose fraction f_c , given accurately by $\lambda(f_c) = 1456 + 97.9f_c - 119f_c^2 + 54f_c^3 - 4.5f_c^4$, and is very insensitive to changes in lignin concentration for .5 $\leq f_c \leq$ 1.0. For example, suppose the spectral sampling interval $\Delta\lambda$ is that of AVIRIS, 10 nm, and that three perfect spectral band determinations are possible at 1484 and 1474 and 1464 nm. The minimum resolvable difference in lignin concentration Δf_c is approximately 0.75 between the first pair of these and about 0.10 between the second pair. A similar relationship, spectrally less well defined, prevails for the complex of bands between 1650 and 1850 nm.

We return now to interpretation of band positions of $R_{d\,\omega}$ in Figure 1. From the regression formula for $\lambda(f_c)$ a reflectance minimum at 1460 nm implies a lignin concentration in the two-component dry mix of 94%, and a similar abundance from the band near 1775 nm. This exceeds by far the expected lignin abundance in plant materials of 10- 35% dry weight (Crawford, 1981).

Other chemical constituents in addition to lignin and cellulose make spectral contributions to the desiccated foliar reflectance, and will alter by dilution the relative abundances of lignin and cellulose present. The nature of the spectral contributions so introduced will be described qualitatively using hypothetical two-component systems, cellulose-starch and cellulose-protein (D-ribulose 1 -5-d iphosphate carboxylase), illustrated in Figures 3 and 4. Combinations with other plant chemical constituents might be worked out from spectral data given by Elvidge (1990). The admixing of starch with cellulose displaces the 1485-nm cellulose band to shorter wavelengths, similar to lignin. The 1775-nm band position is largely unaffected. The admixing of protein with cellulose produces displacements opposite (but of comparatively small magnitude) to those of both starch and lignin at 1485 nrn and to shorter wavelengths at 1775 nm, also similar to that of lignin. Thus both protein and starch mimic spectrally the presence of lignin in mixes with cellulose, especially at 1775 nrn. The isolation of lignin concentration from band position alone without knowledge of other end member concentrate ions thus seems problematical.

- 2. **Mixing of desiccated and** liquid water components. Mixing relationships employed in the present application of KM theory together with spectral reflectance of mixtures based thereon have been worked out to isolate signatures of supposed desiccated leaf components and to aid interpretation of spectral signatures of derived reflectance residuals. The theory applied to leaf reflectance awaits detailed experimental validation but offers another set of relationships that suggest its usefulness. We used the intrinsic k- and s-functions of Figure 1 in Part 1 of this article together with Equations (1) and (2) to calculate for sweetgum the spectral reflectance of intermediate mixtures of wet and dry components. These calculations are illustrated in Figure 5. A comparison with single leaf reflectance data as a function of relative water content given by Hunt and Rock (1989) is suggestive.
- **3. Reflectance retrieval** from **AVIRIS.** The previous analysis leading to plots of residuals given in Figure 4 in Part 1 was based on diffuse spectral reflectance

measurements made under idealized conditions with a laboratory spectrometer. The largest spectral variations in these residuals amount to approximately 2 % in the 1700-nm region, Reflectance variations are also present below this level. Under field conditions, using measurements of the upwelling radiance at AVIRIS, an atmospheric model is ordinarily required to retrieve an effective surface (Lambertian) reflectance, unless ground targets can be used (Elvidge, 1988). Noise arising from spatial fluctuations or uncertainties in atmospheric properties and from AVIRIS will contribute uncertainty to the reflectance values so derived. We carried out numerical experiments with the LOWTRAN 7 (Kneizys et al., 1983) radiative transfer model to estimate uncertainties due to atmospheric variations, It proves advantageous to recalibrate AVIRIS in-flight using local surface targets to eliminate channel-to-channel variations in radiance that are thought to originate from changes in the radiometric calibration coefficients between laboratory and in-flight conditions,

For homogeneous, plane-parallel atmospheric conditions over uniform ground of 1 ambertian surface reflectance ρ_s , the radiance at AV1 RIS is represented approximately as

$$I(\mu,\mu_0,\tau) = \frac{F_0}{4\mu} \left[S(\mu,\mu_0,\tau) + \frac{4\rho_g}{1-\rho_g \bar{s}} \mu \mu_0 T(\mu,\mu_0,\tau) \right]$$
(3)

In Equation (3) πF_O is the solar irradiance, $S(\mu, \mu_0, \tau)$ is the atmospheric scattering function, $T(\mu, \mu_0, \tau)$ is the two-way diffuse plus direct atmospheric transmittance, \overline{s} is the hemispherical backscatter function, μ and μ_0 are cosines of the zenith angles of viewing and solar incidence directions respectively, and τ is optical depth. Spectral dependence of the atmospheric and surface quantities is implied. An in-flight calibration experiment redefines the radiometric calibration in terms of in-flight coefficients Φ^{\bullet} given by

$$\Phi^* = \frac{(L_M)_c}{(DN - DN_0)_c} \tag{4}$$

where DN and DN₀ represent instrument and dark current response for the conditions of calibration, and $(L_m)_c$ is the radiance at AVIRIS obtained from a radiative transfer model (I OWTRAN and/or MODTRAN) using measured atmospheric conditions. $(L_m)_c$ is given approximately by

$$(L_m)_c \sim \left[\frac{S_c}{4\mu_c} + (\mu_0)_c T_c R_c + (\mu_0)_c T_c \overline{S}_c R_c^2\right] F_{\odot}$$
 (5)

With the in-flight calibration factors, the ground reflectance R_{ϱ} is

$$R_{g} = -\frac{A}{B} - \overline{s} \left(\frac{A}{B}\right)^{2} + \left[1 + 2\overline{s} \left(\frac{A}{B}\right)\right] \frac{\Phi^{*}}{B} (DN - DN_{0}) - \overline{s} \frac{\Phi^{*2}}{B^{2}} (DN - DN_{0})^{2}$$
 (6)

where (DN - I] NO) represents the dark-current corrected in-flight instrument response, and

$$A = \frac{SF_{\odot}}{4\mu'} \quad B = \mu_0 TF_{\odot}$$

The expression for R_g , Equation (6) is independent of the solar irradiance, but use of the in-flight calibration coefficients Φ^* has introduced additional variables pertaining to atmospheric conditions (luring calibration and also the calibration target reflectance R_e . We applied standard error propagation formulas to Equation (6) to evaluate a fractional uncertainty σ_{R_g}/R_g from fluctuations in all the atmospheric parameters (taken equal for both calibration and observation experiments) and from the AVIRIS response parameterized as the signal/noise ratio. The LOWTRAN model evaluated was midlatitude summer, rural aerosols, surface meteorological range 25 km, surface reflectance 0.50, and solar zenith angle 22°,179. The calculated uncertainty as a function of AVIRIS signal/noise ratio at 1700 ntn with prescribed atmospheric uncertainties, written collectively as us/a to represent σ_S/S , etc., are shown in Figure 6, Values of σ_{R_g}/R_g less than a few percent are achieved only for uniform atmospheric conditions ($\sigma_a/a < .01$) and high signal/noise ratios (> 100).

- 4. Summary. We used the Kubelka-Munk theory of diffuse spectral reflectance in layers to analyze influences of multiple chemical components in leaves. As opposed to empirical approaches to estimation of plant chemistry, the full spectral resolution of laboratory reflectance data was retained in an attempt to estimate lignin or other constituent concentrations from spectral band positions. A leaf water reflectance spectrum was devised from theoretical mixing rules, reflectance observations, and calculations from theory of intrinsic k- and s-functions. Residual reflectance bands were then isolated from spectra of fresh green leaves. These proved hard to interpret for composition in terms of simple two component mixtures such as lignin and cellulose. We next investigated spectral and dilution influences of other possible components (starch, protein). These components, among others, added to cellulose in hypothetical mixtures, produce band displacements similar to lignin, but will disguise by dilution the actual abundance of lignin present in a multicomponent system. This renders interpretation of band positions problematical. Knowledge of end-members and their spectra, and a more elaborate mixture analysis procedure may be called for (see, for example, Kortum, 1969, p. 303). Good observational atmospheric and instrumental conditions and knowledge thereof are required for retrieval of expected subtle reflectance variations present in spectra of green vegetation.
- 5. Acknowledgments. We thank Chris Elvidge of Desert Research Institute, Reno, Nevada, for use of his reflectance data. Conversations with Dr. Barry Prigge, Botany Dept., UCLA, are also gratefully acknowledged. This article presents results of research at Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA,

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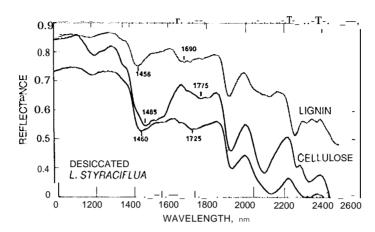


Figure 1. Reflectance of lignin, cellulose, and desiccated *L. styraciflua*.

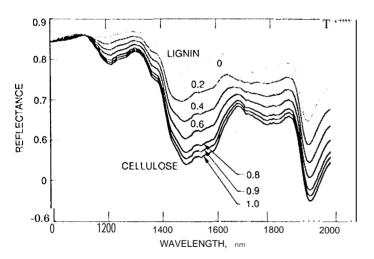


Figure 2. Reflectances of hypothetical mixes of cellulose and lignin. Curves are for cellulose fractions of 1.09 pure cellulose), 0.9, 0.8, 0.6, 0.4, 0.2, and 0.0 (pure lignin).

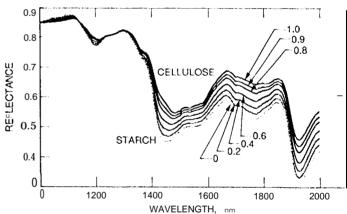


Figure 3. Reflectance of hypothetical mixes of cellulose and starch, See caption Figure 2 for curve assignments.

0.9 0.8 0.9 0.8 0.7 0.0.9 0.0.2 0.0.2 0.0.4 0.0.2 0.0.2 0.0.4 0.0.2 0.0.4 0.0.2

Figure 4. Reflectance of hypothetical mixes of cellulose and protein. See caption Figure 2 for curve assignments.

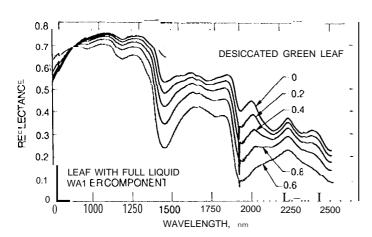


Figure 5. Reflectance of hypothetical combinations of desiccated *L. styraciflua* and leaf liquid water components.

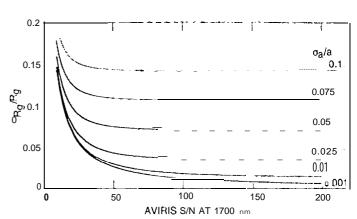


Figure 6. Calculated uncertainties in retrieved surface reflectance for AVIRIS S/N and atmospheric variability.